PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
A61K 7/42, 7/44

A1

(11) International Publication Number: **WO 99/33439**

(43) International Publication Date: 8 July 1999 (08.07.99)

(21) International Application Number: PCT/US98/27433

(22) International Filing Date: 22 December 1998 (22.12.98)

(30) Priority Data:

08/998,238	24 December 1997 (24.12.97)	US
09/113,815	10 July 1998 (10.07.98)	US

(71) Applicant *(for all designated States except US)*: SHAKLEE CORPORATION [US/US]; Shaklee Terraces, 444 Market Street, San Francisco, CA 94111 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: GREENE, James, A. [US/US]; 991–6 Asilomar Terrace, Sunnyvale, CA 94086 (US). SIDDIQUI, Mukhtar [US/US]; 3172 Riviera Way, San Ramon, CA 94583 (US). ROBERTS, Richard, L. [US/US]; 1977 Kostka Lane, Germantown, TN 38139 (US).

(74) Agent: NOONAN, William, D.; Klarquist, Sparkman, Campbell, Leigh & Whinston, LLP, Suite 1600, One World Trade Center, 121 S.W. Salmon Street, Portland, OR 97204 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: COMPOSITION WITH HIGH EFFICIENCY SKIN PROTECTION FROM DAMAGING EFFECTS OF ULTRAVIOLET LIGHT

(57) Abstract

A topical antioxidant composition for the protection of skin from damage caused by ultraviolet radiation. The composition includes a first component (such as beta glucan or grape seed extract) that increases cellular viability of epidermal cells, and a second component that decreases the production of inflammatory mediators, such as prostaglandins, in those cells. In a particular embodiment, the composition includes beta glucan in combination with panthenol, grape seed extract, vitamin C and superoxide dismutase, which exhibit a synergistic effect in protecting the skin from the adverse effects of ultraviolet radiation. In another embodiment, the composition further includes Vitamin A and Vitamin E. In a further embodiment, the composition includes a combination of one or more antioxidants and sunscreen agents in an emulsion, such as water–in–oil (W/O) emulsion, which provides superior protection of the skin against the harmful effects of ultraviolet radiation. The antioxidant compositions are incorporated into sunscreen products, soap, moisturizing lotions, skin toners, and other skin care products.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

COMPOSITION WITH HIGH EFFICIENCY SKIN PROTECTION FROM DAMAGING EFFECTS OF ULTRAVIOLET LIGHT

FIELD OF THE INVENTION

This invention concerns a topical antioxidant composition for the protection and treatment of human skin, particularly skin that is exposed to harmful ultraviolet radiation.

BACKGROUND OF THE INVENTION

The ultraviolet (UV) wavelengths of sunlight can cause sunburn (erythema) and blistering (edema). Exposure to ultraviolet light can also cause the skin to feel dry and taut in moderate doses, and to peel if exposed to higher doses. These acute, or short term, effects are readily perceptible. However, there are also more subtle acute effects that are not as readily discernable, such as photo-immunosuppression, cross-linking of deoxyribonucleic acid (DNA), formation of sunburn cells, and loss of Langerhans cells. Even more serious long term effects can occur, such as skin cancer and premature aging of the skin.

Sunscreen products are known to protect the skin from some of the harmful effects of ultraviolet light exposure. These products contain molecules that absorb the harmful wavelengths of ultraviolet light before they can reach the skin. The absorbed light is converted to heat and rapidly dissipated to the skin and environment, which allows these molecules to revert to a lower energy state, and subsequently absorb another photon of light. In this manner, sunscreen agents can absorb numerous photons of ultraviolet light in a relatively short period of time. By absorbing the harmful wavelengths of light, sunscreen products prevent many of the acute and chronic effects caused by ultraviolet light.

However, sunscreen products are not perfect in their mode of action. No single sunscreen agent is capable of absorbing all of the harmful wavelengths striking the skin. Higher Sun Protection Factor (SPF) formulations address this problem by including a combination of sunscreen agents in the formulation. However, even when using a combination of sunscreen agents, these products do

not provide complete protection, particularly from the longer ultraviolet wavelengths. Although these longer wavelengths do not readily elicit many of the acute damaging effects commonly attributed to ultraviolet light exposure, recent research indicates that these wavelengths can create free radicals in the skin. These free radicals may be responsible for the premature aging of the skin commonly linked to ultraviolet light exposure.

The skin possesses defense mechanisms against the generation of ROS. These defenses include the presence of enzymes such as superoxide dismutase, catalase, glutathione transferase, glutathione peroxidase and glutathione reductase, as well as antioxidants such as tocopherols, ubiquinone, ubiquinol, ascorbic acid and dehydroascorbic acid. Unfortunately, ultraviolet light entering the skin can easily overwhelm these defense systems, such that the amount of superoxide dismutase and glutathione transferase in the skin declines significantly upon irradiation with solar simulated ultraviolet light. Simultaneous with the loss of these reducing enzymes, there is a dramatic increase in conjugated double bonds formed in the skin from the linoleates present in cell membranes. There is also an increase in thiobarbituric acid reactive substances present in the skin, which represent a collection of molecules that are formed from ROS. Prostaglandins are a mediator of inflammation that is believed to be produced by skin damage, and ROS may create conditions that promote the formation of prostaglandins and sunburn cells.

The effectiveness of sunscreen products is expressed as a SPF value. A SPF value is recognized as the ratio of the irradiation time required to elicit a minimum erythemal reaction (sunburn) on sunscreen protected skin using a solar simulator, to the irradiation time required to elicit the same minimum erythemal reaction (sunburn) on unprotected skin. This test is conducted under clinical conditions according to the procedure described in the Proposed Monograph for Sunscreen Containing Drug Products (hereafter referred to as the Proposed Monograph) published by the U.S. Food and Drug Administration (FDA) in the U.S. Federal Register, Vol. 43, August 25, 1978, Part 2, pages 38206-38269, which is incorporated by reference. As used herein, the term "SPF" or Sun

Protection Factor is defined in accordance with the definitions in the Proposed Monograph. This same publication also describes the clinical testing procedure mandated for determining whether sunscreen products are waterproof, water resistant and sweatproof.

The labeled SPF values are generally recognized as being between 2 and 50. This is not meant to imply that SPF values greater than 50 are unachievable given the previous formulation technology. However, the amounts of sunscreen agents needed to achieve such high SPF values are usually cost prohibitive given current formulation technologies. The concentration of sunscreen agents needed to satisfy a "waterproof" designation are particularly high, because some of the agents are washed away in the test that measures SPF for a waterproof composition.

A waterproof product is one that exhibits its labeled SPF value after 80 minutes of exposure to water under conditions that simulate swimming for that period of time. A water resistant product is similarly defined, except that it must withstand 40 minutes of water exposure. Although there is a separate test for the sweatproof claim, the Proposed Monograph allows products that pass the waterproof or water resistant claim to also carry the sweatproof claim.

The most common sunscreen products sold in today's market are oil-in-water emulsions incorporating stearic acid neutralized with triethanolamine. The SPF values of such emulsions range from 2 to 50, and they commonly include ethylhexyl methoxycinnamate as the sunscreen agent. As the SPF of these formulations increases, they commonly contain ethylhexyl salicylate, homosalate, octocrylene and/or oxybenzone in addition to the ethylhexyl methoxycinnamate mentioned above. Alternatively, padimate O can be used in place of the ethylhexyl methoxycinnamate or the salicylates mentioned above. Dioxybenzone, avobenzone or menthyl anthranilate can be used in place of oxybenzone. If the product does not claim to be substantive to the skin (*i.e.*, waterproof or water resistant), trolamine salicylate or DEA methoxycinnamate can be used in place of (or in combination with) the ethylhexyl methoxycinnamate, ethylhexyl salicylate or homosalate. Additionally, sulisobenzone may be used in such non-substantive

formulations in place of oxybenzone. The Proposed Monograph lists 21 active ingredients that can be used individually or in combinations to achieve the desired product SPF.

In addition to emulsion (lotion and/or cream) formulations, suncare products can be found in almost any desired form, such as oils, sticks, gels, ointments and pastes. The SPF of these product forms are dependent upon the sunscreen agents employed, their concentration in the formulation, and the content as well as type and amount of any volatile components in the formulation (such as water, alcohol, and volatile oils).

The most popular sunscreen products sold in the market today are TEA stearate based oil-in-water lotion formulations exhibiting SPFs of 15 and above. Most of the SPF 15 formulations contain approximately 7.5% ethylhexyl methoxycinnamate and 4.0% oxybenzone. By judiciously modifying these SPF 15 formulations, and adding approximately 5.0% octyl salicylate to the sunscreen mixture, the SPF values can be increased to a value of about 30. By further modification, including the addition of 8.0% octocrylene, SPF values of up to 50 can be obtained.

An emulsifier technology from Goldschmidt Chemical Company uses a silicone emulsifier which can be used to formulate water-in-oil lotion products. An example of this emulsifier is Abil EM 90, which is a nonvolatile silicone oil that includes cetyl dimethicone copolyol. Another example of this emulsifier is Abil WE 09, which is a nonvolatile silicone oil that contains polyglyceryl-4-isosterate, cetyl dimethicone copolyol and hexyl laurate. The chemical structures of such emulsifiers are disclosed in U.S. Patent No. 5,482,714, which is incorporated by reference, and which describes use of the emulsifier in a skin protectant emulsion.

U.S. Patent No. 5,447,715 discloses that volatile silicone oils can be used to improve the SPF value of a non-aqueous waterproof sunscreen composition, but such a non-aqueous product would be unsuitable to formulate aqueous emulsions.

Vitamins have been reported to have antioxidant properties. Antioxidants are materials capable of blocking the biochemical cascade of inflammatory

mediators produced by free radicals. Compositions that incorporate Vitamins A or E, or their derivatives, in sunscreen compositions, are shown in U.S. Patent Nos. 4,454,112; 5,532,805; and 5,378,461. The use of Vitamin C in combination with Vitamins A, E, B and other agents in a skin protectant composition, is described in U.S. Patent No. 4,938,960. An antioxidant preparation that is said to protect the skin against harmful ultraviolet radiation is disclosed in U.S. Patent No. 5,607,921, and contains Vitamin C, in combination with Vitamins A and E, and monosaccharide or amide precursors. Sunscreen compositions containing panthenol and other agents are disclosed in U.S. Patent Nos. RE 33,845; 5,505,935; 5,445,823; and 5,573,754. The antioxidant effect of superoxide dismutase when externally applied to the skin to protect against the effects of ultraviolet radiation is also described in U.S. Patent No. 5,601,806.

In spite of advances in recent years in the protection of skin from harmful ultraviolet radiation, the epidemic of skin cancer and skin damage from the effects of this radiation has continued unabated. The loss of portions of the ozone layer from environmental pollution is believed to have contributed to an increase in ambient ultraviolet radiation that reaches exposed skin. Many skin protection preparations that could prevent sun damage have an unacceptable odor or texture that discourages their more frequent use, and many of the available skin protectants do not sufficiently protect the skin from these many mechanisms of injury. Hence there is a significant public health need for commercially acceptable or improved preparations that can be topically applied to human and animal skin, to offset the harmful effects of ultraviolet radiation.

SUMMARY OF THE INVENTION

The present invention provides a therapeutic or cosmetic composition containing new antioxidants, or agents that reduce sun induced skin damage and inflammation by aborting the production of prostaglandins in the skin. The composition has a superior therapeutic or cosmetic effect. Certain embodiments provide more protection from the adverse effects of ultraviolet light, without

having to include excessive concentrations of sunscreen agents in a protective formulation.

The invention includes a composition and method for inhibiting skin damage induced by ultraviolet radiation, by applying topically to the skin an antioxidant composition which includes beta glucan or grape seed extract in a sufficient amount to protect the skin from damaging effects of ultraviolet radiation. In disclosed embodiments, the composition includes panthenol, beta blucan, grape seed extract, Vitamin C (and its analogues, such as magnesium ascorbyl phosphate, ascorbyl palmitate, etc.), and superoxide dismutase, which act synergistically to improve cellular viability and reduce the production of inflammatory prostaglandin PGE_2 in skin exposed to ultraviolet radiation. The composition can also include Vitamin A (retinol and its analogues, such as retinyl palmitate) and Vitamin E (tocopherol and its analogues, such as tocopheryl acetate), which also act synergistically as an antioxidant in the skin. Further embodiments take advantage of the surprising finding that a mixture of one or more antioxidants and sunscreen agents in an emulsion, such as a water-in-oil (W/O) emulsion, exhibits unexpectedly superior protection of the skin against the detrimental effects caused by exposure to ultraviolet radiation.

In particular embodiments, the composition includes at least 0.005% beta glucan, 0.005% panthenol, 0.00001% grape seed extract, 0.0001% Vitamin C, and 0.0001% superoxide dismutase. For example, the composition may contain 0.005-5.00% beta glucan, 0.005-5.00% panthenol, 0.00001-1.00% grape seed extract, 0.0001-3.00% Vitamin C, and 0.0001-1.0000% superoxide dismutase. The composition may further include at least 0.0005% Vitamin A, and at least 0.05% Vitamin E, for example 0.0005-0.50% Vitamin A, and 0.05-30.00% Vitamin E. All percent compositions are given by weight in this specification.

In more specific embodiments, the topical composition includes beta glucan and/or grape seed extract in a sufficient amount to improve cellular viability in the skin when applied topically before or after exposure to ultraviolet radiation, and at least one other skin protectant that reduces skin damage caused by ultraviolet light. When beta glucan is chosen, the skin protectant may be selected from the

group consisting of one or more of panthenol, grape seed extract, Vitamin C, superoxide dismutase, Vitamin A or Vitamin E in a sufficient amount to reduce production of PGE_2, or increase cellular viability, in the skin when applied topically. The Vitamin C may be in the form of magnesium ascorbyl phosphate, while the Vitamin A may be in the form of Vitamin A palmitate, and the Vitamin E may be in the form of Vitamin E acetate.

The invention also takes advantage of the surprising finding that a mixture of an antioxidant and a sunscreen in an emulsion, such as a water-in-oil (W/O) emulsion, exhibits unexpectedly superior protection of the skin against the detrimental effects caused by exposure to ultraviolet radiation. Another embodiment of the antioxidant composition is therefore a composition which comprises (or consists essentially of) the antioxidant, a sunscreen, and a sufficient amount of a non-volatile emulsifier (such as an organopolysiloxane, for example an alkylpolysiloxane, such as an alkyl dimethicone emulsifier, including a polysiloxane polyalkyl polyether copolymer) that enhances a sun protection factor (SPF) of the composition. The composition may comprise, for example, a low level of sunscreen agent (or agents) in combination with a mixture of antioxidants in a water-in-oil organopolysiloxane and polyglycerol fatty acid ester emulsion.

In particular embodiments, the sunscreen includes one or more agents selected from the group of ethylhexyl methoxycinnamate, DEA methoxycinnamate, padimate O, ethylhexyl salicylate, homosalate, TEA salicylate, oxybenzone, dioxybenzone, sulisobenzone, avobenzone, octocrylene, titanium dioxide, zinc oxide or menthyl anthranilate. In other embodiments, the sunscreen includes at least one UVA sunscreen agent selected from the group of oxybenzone, dioxybenzone, sulisobenzone, avobenzone or zinc oxide, and at least one UVB sunscreen agent, selected from the group of ethylhexyl methoxycinnamate, DEA methoxycinnamate, padimate O, ethylhexyl salicylate, homosalate, TEA salicylate, octocrylene or titanium dioxide. In other specific embodiments, the sunscreen comprises at least oxybenzone and at least one of ethylhexyl methoxycinnamate and octyl salicylate. The antioxidant in the composition may include a mixture of one or more of the individual antioxidants described above.

In particular embodiments, the composition is a sun-protective preparation in the form of an emulsion, wherein the composition is at least 50% water, and the emulsifier includes 1-12 % of an emulsification system that includes cetyl dimethicone copolyol, and the sunscreen agent and antioxidant are present in an amount sufficient to maintain the SPF of the composition at a value greater than about 15, or even 30 or greater. In particular embodiments, the sum of the SPF values of the antioxidant and sunscreen components tested separately is no more than about 70% (for example no more than 50% or 60%) of the SPF value of the sunscreen components tested together.

The invention also includes an ultraviolet radiation protective composition, comprising about 0.0002-4% of a lipid soluble antioxidant component that includes Vitamin A and Vitamin C, about 0.004-5% of a water soluble component that includes Vitamin C, beta glucan, grape seed extract, and superoxide dismutase, and a sunscreen component that contains less than about 12% of sunscreen agents, and an emulsifier. In particular embodiments of the composition the emulsifier is a polyalkylsiloxane, and may further include hexyl laurate and an ester, such as a polyglyceryl isostearate.

The invention also includes a method of improving an SPF value of a formulation for protecting skin from the harmful effects of ultraviolet radiation, by combining one or more antioxidants with one or more sunscreen agents, in the presence of an emulsifier, such as a water-in-oil emulsion, for example an organopolysiloxane emulsifier, sufficient to enhance the SPF value of the formulation to greater than (for example at least 10 percent, 20 percent, or even 40% more than) the sum of the SPF value of the antioxidants and sunscreen agents alone. The invention also includes a method of protecting skin from the effects of ultraviolet radiation, by applying the emulsion of one or more sunscreen agents and one or more antioxidants to the skin prior to exposure to ultraviolet radiation.

The composition of the present invention, however, may be provided in many forms, such as an aqueous or non-aqueous solution, suspension or an emulsion (water-in-oil or oil-in-water). The composition may be a skin toner composition, a moisturizing lotion, a sunscreen composition, a skin cleanser, or

any other skin treatment composition. The composition may also be used in methods of protecting skin against the harmful effects of ultraviolet radiation, by applying topically to the skin an amount of the composition effective to reduce the production of PGE_2 in the skin, or improve cellular viability. The composition may be applied before or after exposure to the sun, but is preferably applied prior to sun exposure, for example immediately before sun exposure.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description of several embodiments.

DETAILED DESCRIPTION

The combination of antioxidants in the present composition provides unexpectedly superior protection against the damaging effects of ultraviolet light exposure to that provided by the individual antioxidants. Furthermore, the present invention takes advantage of the surprising finding that a mixture of one or more of the antioxidants and sunscreen agents synergistically combine in a water-in-oil emulsion to provide unexpectedly superior protection to the skin against the harmful effects of ultraviolet radiation.

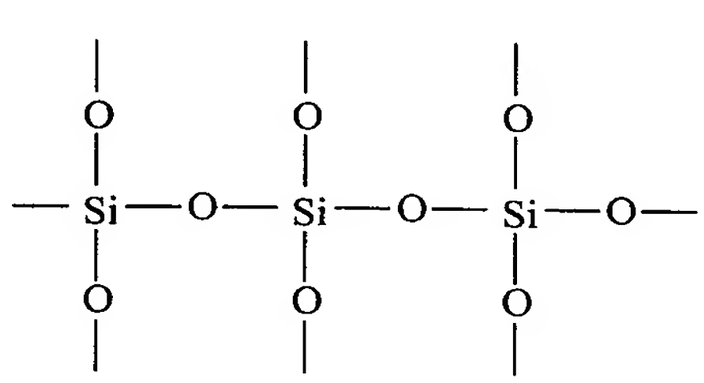
In some of the embodiments disclosed in the examples below, it is shown that a mixture of antioxidants exhibits more antioxidant activity than any of the individual antioxidant materials tested alone. In particular embodiments, it is also shown that this synergistic combination of antioxidants may be incorporated into a water-in-oil emulsion formulation that exhibits SPF values which far exceed SPF values that would be expected given the low concentration of sunscreen agents present in the formulation. The particular combination of antioxidants, and the low level of sunscreen agents in this water-in-oil emulsion system, are unexpectedly synergistic as measured by SPF values.

The sunscreen agents employed in the formulations are the same combinations used in some traditional formulations, such as ethylhexyl methoxycinnamate and oxybenzone. However, the levels of these sunscreen agents are significantly lower than those of more traditional oil-in-water suncare

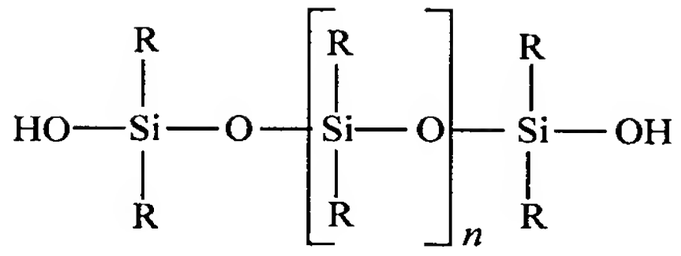
product formulations. Additionally, the combination of antioxidants employed in the formulations covered by this technology is unique. The antioxidant combination includes a mixture of beta glucan, Vitamin E acetate, Vitamin A palmitate and magnesium ascorbyl phosphate (stabilized Vitamin C), panthenol, grape seed extract and superoxide dismutase. The effect that this combination of antioxidants has upon the skin, as measured by its free radical scavenging activity, and the low SPF of the emulsion when combined with sunscreen agents, is novel and unexpected.

As used herein, an "antioxidant" is a compound that reduces the inflammatory biochemical cascade initiated by reactive oxygen species. Antioxidants include, for example, Vitamin C and Vitamin E (and their esters), magnesium ascorbyl phosphate, panthenol, beta glucan, grape seed extract, superoxide dismutase, and mixtures of one or more of these individual antioxidant agents.

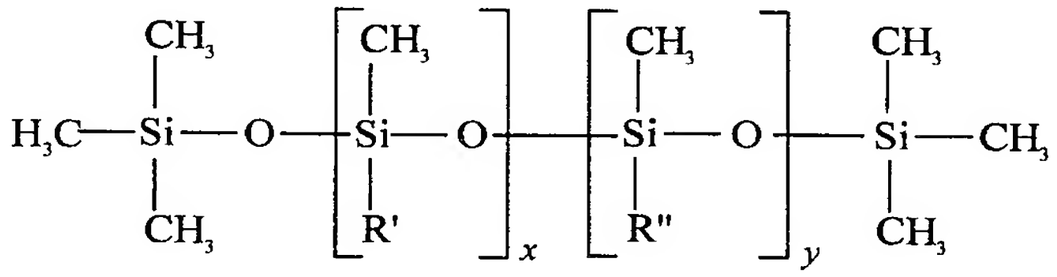
A "non-volatile" siloxane includes an organopolysiloxane that has a flash point of at least about 200°F. Hence a cetyl dimethicone polyol, such as ABIL WE09 (which has a flash point of 255°F.) would be a nonvolatile siloxane. A "siloxane" is a straight chain compound (analogous to paraffin hydrocarbons) containing silicon atoms bonded to oxygen and so arranged that each silicon atom is linked with four oxygen atoms:



A "silicone" or "polyorganosiloxane" is an organosilicon polymer containing chains of alternating oxygen and silicon atoms with substituent organic groups, frequently methyl or phenyl, attached to each silicon atom, as described for example in *Remington: The Science and Practice of Pharmacy*, 19th edition, pages 867-868, and as shown below:



In particular embodiments, the emulsifier is a non-volatile silicone oil, for example a polysiloxane polyalkyl polyether copolymer, also known as copolyols, having a molecular weight from 10,000 to 50,000, which are disclosed for example in U.S. patent No. 5,746,945, which is incorporated by reference, and



include:

wherein the groups R' are each chosen from –H and C_{1-18} alkyl, and R" is – $[CH_2CH_2O]_a[CH_2(CH_2)CHO]_bH$, in which a is 9 to 115, b is 0 to 50, x is 133 to 673, and y is 0.25 to 25. In particular embodiments, a is 14, b is 13, x is 249 and y is 1.25.

The emulsifier can also include a dimethicone selected from alkyl- and alkoxy-dimethicone copolyols, such as those disclosed in U.S. Patent Application No. 5,659,523, which is incorporated by reference. A particularly preferred copolyol is cetyl dimethicone copolyol, available from T.H. Goldschmidt as Abil EM-90, or Abil WE-09 (which also contains polyglyceryl-4-isostearate and hexyl laurate).

The term "aqueous" means that the composition is not substantially free of water. An emulsion is a dispersed system containing at least two immiscible liquid phases. An emulsion in which water is the dispersed phase and oil is the dispersion medium is a "water-in-oil" emulsion. An "aqueous emulsion" refers to an emulsion that contains water as one of its phases.

A "sunscreen agent" is an agent that, in an effective amount, reduces the amount of skin erythema by blocking exposure to ultraviolet radiation, as determined (for example) by the procedures set forth in the Proposed Monograph. The sunscreen agent can protect against either UV-B type ultraviolet radiation or UV-A type ultraviolet radiation, or both. In particularly disclosed embodiments, the sunscreen agent is an aromatic compound (such as oxybenzone and cinnamic acid derivatives) which efficiently absorb harmful ultraviolet rays, and is substantially free of particulate sunscreens such as ZnO or TiO_2, or other metal oxides that may have an adverse effect on the stability of the antioxidant agents in the composition. Particular embodiments of the composition also exclude copper or iron, that may also have adverse effects on stability.

Typical suitable UV-B type sunscreening agents include substituted para-aminobenzoates , e.g., octyl dimethyl PABA, available from Van Dyk & Co., Inc., Belleville, N.J. 07109 under the tradename Escalol 507 and usually present in the range of about 0 to 8 weight percent (for example 1.5 to 8 weight percent); alkyl esters of para-methoxycinnamate, e.g., octyl para-methoxycinnamate, available from Givaudan Corp., Clifton, N.J. 07104 under the tradename Parasol MCX and usually present in the range of about 0 to 7.5 weight percent (for example 1.5 to 7.5 weight percent); and certain esters of salicylic acid, e.g., homomenthyl salicylate, usually in the range of about 0 to 15 weight percent (for example 4 to 15 weight percent)or octyl salicylate, usually in the range of about 0 to 5 weight percent (for example 3 to 5 weight percent). (All weight percents are weight percent of total sunscreen composition.)

Typical suitable UV-A type sunscreening agents include benzophenone-3 usually present in the composition in the range of about 0 to 6 percent (for example 0.5 to 6 percent) and available from American Cyanamid Co., Wayne, N.J. 07470 under the tradename Spectra-Sorb UV-9; benzophenone-8, usually present in the composition in the range of 0 to 3 weight percent (for example 0.5 to 3 weight percent) and available from American Cyanamid Co. under the tradename Spectra-Sorb UV-24; and menthyl anthranilate, usually present in the composition in the range of about 0 to 5 weight percent (for example 3.5 to 5

weight percent) and available from Haarmann and Reimer (N.J.) under the tradename Sunarome UVA.

The compositions of the present invention preferably contain at least one UV-B type sunscreening agent and at least one UV-A type sunscreening agent. The compositions of the present invention may also contain perfumes, preservatives, dyes, softeners, physical reflectors and other antioxidants, as well as any other class of materials whose presence may be cosmetically or otherwise desirable.

Other antioxidants include propyl, octyl and dodecyl esters of gallic acid, butylated hydroxyanisole (usually as a mixture of ortho and meta isomers), butylated hydroxytoluene and nordihydroguaiaretic acid. Typical suitable preservatives include the lower alkyl esters of para-hydrobenzoates (parabens) especially, methyl paraben, ethyl paraben, propyl paraben, butyl paraben, isobutyl paraben and mixtures thereof, and benzoic acid. Typical suitable perfumes include any oil soluble perfume or fragrance or mixture of perfumes or fragrances well known to those skilled in the art. Typical suitable physical reflectors include talc, kaolin, chalk, precipitated silica, zinc oxide, and titanium dioxide.

The compositions of the present invention may be in the form of a liquid, gel or semi-solid. The selection of ingredient type and amount is dictated by the nature of the composition, i.e. gel or semi-solid, and is within the skill of cosmetic chemists. For example, larger amounts of wax are incorporated into the semi-solid compositions of the present invention than into the liquid ones.

The term "waterproofing effective amount of at least one waterproofing agent" means that if a waterproofing agent is used , the waterproofing agent(s) is present in the composition at a concentration of at least 0.3 percent, and for example in the range 0.3 – 3 percent. Typical suitable waterproofing agents include copolymers derived from polymerization of octadecene-1 and maleic anhydride, for example using procedures such as those disclosed in U.S. Patent No. 3,860,700. A particular waterproofing agent is a copolymer commercially available from Chevron Chemicals Co. under the tradename PA-18 polyanhydride

resin. Others include PVP/Eicosene Copolymer, PVP/Hexadecene Copolymer, and PVA/VA Copolymer, all available from GAF of Wayne, NJ.

Typical suitable cosmetic waxes include ozokerite, lanolin alcohol, paraffin wax, bayberry wax, polyethylene wax, especially AC 617 available from Allied-Signal Corp., Morristown, N.J.; Polawax (a reaction product of higher fatty alcohols and ethylene oxide available from Croda, Inc., New York., N.Y. 10016), trihydroxystearin, lanolin wax, beeswax, Candellila wax, microcrystalline wax, Carnauba wax, cetyl alcohol, stearyl alcohol, spermaceti, cocoa butter, fatty acids of lanolin, mono-, di- and tri-behenate (a triester of behenic acid and glycerine) and C_{18}-C_{36} acid triglyceride (a mixture of triesters of C_{18}-C_{36} carboxylic acids and glycerine), available from Croda, Inc., New York, N.Y., under the tradenames Syncrowax HRC and Syncrowax HGL-C, respectively, fatty esters which are solid at 25°C, silicone waxes such as methyloctadecaneoxypolysiloxane and poly (dimethylsiloxy) stearoxysiloxane, stearyl mono- and diethanolamine, rosin and its derivatives such as the abietates of glycol and glycerol, hydrogenated oils solid at 25°C, and sucroglycerides.

Embodiments that also include volatile silicone oils include cyclomethicones such as Dow Corning 344 Fluid, Dow Corning 345 Fluid, Dow Corning 244 Fluid, and Dow Corning 245 Fluid; as well as Volatile Silicone 7207, a trademark of Union Carbide Corp., Danbury, CT., low viscosity dimethicones, i.e. dimethicones having a viscosity of about 50 cst or less, especially dimethicones such as Dow Corning 0.5-200 cst Fluid (Midland, MI). Cyclomethicone and dimethicone are names given by the Third Edition of the CTFA Cosmetic Ingredient Dictionary to cyclic dimethyl polysiloxane compounds and a mixture of fully methylated linear siloxane polymers end-blocked with trimethylsiloxy units, respectively. Other volatile silicone oils having a low heat of vaporization, such as those available from General Electric Co., Silicone Products Div., Waterford, N.Y. and SWS Silicones Div. of Stauffer Chemical Co., Adrian, MI, can also be used in the compositions of the invention.

Typical suitable cosmetic emollients include mineral oil, especially mineral oils having a viscosity in the range of 50 to 500 SUS, lanolin oil, coconut oil,

cocoa butter, olive oil, almond oil, macadamia nut oil, aloe extract, jojoba oil, safflower oil, corn oil, liquid lanolin, cottonseed oil, and peanut oil. Other suitable cosmetic emollients include Purcellin oil, perhydrosqualene, castor oil, polybutene, odorless mineral spirits, sweet almond oil, calophyllum oil, ricin oil, vitamin E acetate, mineral spirits, the oil of cereal germs, such as the oil of wheat germ, and esters such as isopropyl palmitate, isopropyl myristate, butyl myristate, hexadecyl stearate, decyl oleate, acetyl glycerides, the octanoates and benzoates of (C12-C15) alcohols, the octanoates and decanoates of alcohols and polyalcohols such as those of glycol and glycerol, ricin oleates of alcohols and poly alcohols, such as those of isopropyl adipate, hexyl laurate and octyl dodecanoate.

Cosmetic emollients which are solids or semi-solids at ambient temperatures may be used if admixed with one or more of the cosmetic emollients listed above, in amounts sufficient to provide liquid topical compositions. Such solid or semi-solid cosmetic emollients included hydrogenated lanolin, hydroxylated lanolin, acetylated lanolin, petrolatum, isopropyl lanolate, cetyl myristate, myristyl myristate, myristyl lactate, cetyl alcohol, isostearyl alcohol and isocetyl lanolate.

The following examples of the technology are meant to provide a better understanding of how to make and use the invention. Anyone skilled in the art of formulation will readily recognize other potential variants of the technology, which could be applied to formulations. Therefore, these examples are meant to demonstrate but not limit the scope of the patented technology. Definitions and suppliers of the ingredients used in the following illustrative examples may be found in the CTFA Cosmetic Ingredient Dictionary, published by the Cosmetic, Toiletry and Fragrance Association, Inc., Washington, D.C. 20005, Third Edition, 1982. All proportions are by percent weight, unless indicated otherwise.

EXAMPLE 1

Cellular Viability Assay

This example describes how antioxidant activity was measured using a cellular viability assay. The antioxidant activity of individual and combinations of

antioxidant materials were evaluated in cell cultures using the Epiderm Skin Model (EPI-100) from the Mattek Corporation of Ashland, MA. These cell cultures of neonatal foreskin were cultured in accordance with the manufacturer directions, and were assayed for percent cellular viability by measuring the amount of 3-(4,5-dimethylthazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) dye taken up by the cell cultures. Viable cells take up this dye and convert it to insoluble formazin crystals that reside in the mitochondria of the cells until extracted with alcohol. The amount of MTT converted to extractable formazin crystals is directly proportional to the viability of the cell culture. MTT is measured spectrophotometrically. Cells exposed to UV light at a rate of 1.5 Minimal Erythemal Dose (MED) per hour per square centimeter from a solar simulator (filtered to yield wavelengths in the region of 290-400 nm) in the presence of the antioxidant ingredient or mixtures were used to measure the effect of antioxidants to protect the cell culture from the generation of free radicals. The total dose of ultraviolet light was 31.5 mJ/cm^2.

The controls for this portion of the study were cell cultures without added antioxidants (positive control). All cell cultures were also compared to cultures that were not exposed to UV light and did not include antioxidant agents or blends in order to determine percent cellular viability (negative control). This latter measurement was assumed to be equal to 100% viability. Three cell cultures were run for each antioxidant ingredient, blend or control sample tested. The results for these assays were then averaged.

EXAMPLE 2

PGE_2 Production Assay

This example describes how prostaglandin production was measured using a PGE_2 assay. The cell cultures were evaluated for the production of Prostaglandin E_2 (PGE_2) using an assay kit obtained from PerSpective Diagnostics of Cambridge, MA. As with the assay for percent cellular viability, the cell cultures were exposed to a dose of ultraviolet light at a rate of 1.5 MED per hour per square centimeter from a solar simulator in the presence of the antioxidant

ingredients, blends or controls. The total dose of ultraviolet light was 31.5 mJ/cm^2. These cell cultures were then allowed to stand in normal growth media for 24 hours. After being allowed to grow for that period of time, the cell cultures were assayed for production of PGE_2 using the assay kit from PerSpective Diagnostics. The controls for this portion of the study were cell cultures exposed to the same dose of ultraviolet radiation but without added antioxidants (positive control). Three cell cultures were run for each antioxidant ingredient, blend or control sample tested. The results for these assays were then averaged.

The results of these tests from Examples 1 and 2 are shown in Tables 1 and 2. The results shown in Table 1 indicate that all of the antioxidant agents and blends of these agents exhibit significant protective effect from ultraviolet light induced free radicals as measured by percent cellular viability. This activity must be as a result of the antioxidant effect because none of these agents exhibit any significant absorption in the solar ultraviolet wavelengths (290 to 400 nm) at the concentrations tested. Percent cellular viability after light exposure for blends A, B, and C is found in the data presented in Table 3. Although there are some statistically significant differences between individual antioxidant ingredients, the primary statistical differences are found between the blends of the agents and the individual agents composing the blends. For example, Blend B, composed of beta glucan, DL panthenol, grape seed extract, magnesium ascorbyl phosphate and superoxide dismutase, provides statistically superior protection to each of its individual components other than DL panthenol (data not shown). It might have been statistically superior to DL panthenol if the standard deviation of this antioxidant agent had been smaller. Blend A, composed of Vitamin E Acetate and Vitamin A palmitate, provides statistically superior protection when compared to its constituent ingredients at the 90% confidence level.

TABLE 1

Percent Cellular Viability Resulting from UV Light Exposure

Antioxidant Agent Tested	Average Percent Viability ± Standard Deviation	Statistically Different from UV Irradiation Only (Confidence Level)[1]
Beta Glucan	43.6 ± 2.78	Yes (95%)
DL Panthenol	46.3 ± 14.9	Yes (80%)
Grape Seed Extract	39.6 ± 0.48	Yes (95%)
Magnesium Ascorbyl Phosphate [2]	45.1 ± 2.34	Yes (95%)
Superoxide Dismutase	43.0 ± 3.30	Yes (90%)
Vitamin A Palmitate	42.0 ± 4.98	Yes (95%)
Vitamin E Acetate	43.6 ± 2.62	Yes (95%)
Blend A[3]	58.7 ± 8.56	Yes (95%)
Blend B[4]	51.1 ± 3.87	Yes (95%)
UV Irradiation Only[5]	28.4 ± 5.15	-

[1] The level of statistical confidence is based upon hypothesis testing using a Student t test.
[2] This is a stabilized form of Vitamin C (Ascorbic Acid).
[3] Blend A is composed of Vitamin A palmitate and Vitamin E acetate.
[4] Blend B is composed of beta glucan, DL panthenol, grape seed extract, magnesium ascorbyl phosphate and superoxide dismutase.
[5] This cell culture was exposed to UV light in the absence of added antioxidant materials.

The data for the assay of the production of PGE_2 are shown in Table 2. These results show that Blends A and B provide statistically significant protection from ultraviolet light when assayed for PGE_2. Production of PGE_2 resulting from ultraviolet light exposure for Blends A, B, and C is shown in Table 4. Blend B provides statistically superior protection from the production of PGE_2 when compared to its constituent ingredients. This statement is also valid for Blend A. Although not as effective as Blend A or Blend B, the PGE_2 produced is also noted to be as low with grape seed extract and magnesium ascorbyl phosphate alone.

TABLE 2

Production of PGE_2 Resulting from UV Light Exposure

Only Antioxidant Agent Tested Level)[1]	Average PGE_2 Produced ± Standard Deviation	Statistically Different from UV Irradiation (Confidence
Beta Glucan	14,900 ± 3630	No
DL Panthenol	18,300 ± 5700	No
Grape Seed Extract	13,300 ± 2640	No
Magnesium Ascorbyl Phosphate [2]	15,100 ± 5390	No
Superoxide Dismutase	22,900 ± 19,500	No
Vitamin A Palmitate	17,400 ± 5720	No
Vitamin E Acetate	26,000 ± 2750	No
Blend A [3]	7140 ± 538	Yes (85%)
Blend B [4]	861 ± 135	Yes (95%)
UV Irradiation Only [5]	22,900 ± 11,000	-

[1] The level of statistical confidence is based upon hypothesis testing using a Student t test.
[2] This is a stabilized form of Vitamin C (Ascorbic Acid).
[3] Blend A is composed of Vitamin A Palmitate and Vitamin E Acetate.
[4] Blend B is composed of Beta Glucan, DL Panthenol, Grape Seed Extract, Magnesium Ascorbyl Phosphate and Superoxide Dismutase.
[5] This cell culture was exposed to UV light in the absence of added antioxidant materials.

Although many of these ingredients have been used in skin care products previously, the combinations are unique. The use of beta glucan to interfere with the production of an inflammatory mediator (such as PGE_2), or to increase cellular viability following exposure to ultraviolet radiation, is also believed to be unique. Furthermore, the finding that these blends of antioxidant agents exhibit superior protection when mixed together is unexpected.

The combination of blends A and B, which is designated as Blend C in Table 3, was shown to provide statistically significant protection against the damaging effects of ultraviolet light using skin cell cultures. A comparison of this blend of antioxidants was found to be similar to the level of protection afforded by its oil and water soluble component blends. Based upon the results shown in Tables 1 and 2, there is evidence that Blend C provides more protection than its

component ingredients. The data obtained from these tests are shown in Tables 3 through 6.

TABLE 3

Percent Cellular Viability Resulting from UV Light Exposure

Antioxidant System	Average Percent Viability ± Standard Deviation	Statistically Different from UV Irradiation Only (Confidence Level) [1]
Blend A [2]	49.0 ± 4.1	Yes (95%)
Blend B [3]	42.0 ± 7.4	Yes (95%)
Blend C [4]	38.2 ± 1.7	Yes (95%)

[1] The level of statistical confidence is based upon hypothesis testing using a Student t test.
[2] Blend A is composed of Vitamin A palmitate and Vitamin E acetate.
[3] Blend B is composed of beta glucan, DL panthenol, grape seed extract, magnesium ascorbyl phosphate and superoxide dismutase.
[4] Blend C is a mixture of Blends A and B.

TABLE 4

Production of PGE_2 Resulting from UV Light Exposure

Antioxidant System	Average PGE_2 Production ± Standard Deviation	Statistically Different from UV Irradiation Only (Confidence Level) [1]
Blend A [2]	4380 ± 545	Yes (95%)
Blend B [3]	2370 ± 352	Yes (95%)
Blend C [4]	2940 ± 123	Yes (95%)

[1] The level of statistical confidence is based upon hypothesis testing using a Student t test.
[2] Blend A is composed of Vitamin A palmitate and Vitamin E acetate.
[3] Blend B is composed of beta glucan, DL panthenol, grape seed extract, magnesium ascorbyl phosphate and superoxide dismutase.
[4] Blend C is a mixture of Blends A and B.

TABLE 5

Statistical Comparison of Percent Cellular Viability Resulting from UV Light Exposure [1]

Antioxidant System	Blend B [3]	Blend C [4]	UV Irradiation Only [5]
Blend A [2]	NSD [6]	95%	95%
Blend B [3]	-	NSD	95%
Blend C [4]	-	-	95%

[1] The values listed in this table are the statistical confidence level of difference based upon hypothesis testing using a Student t test.
[2] Blend A is composed of Vitamin A Palmitate and Vitamin E acetate.
[3] Blend B is composed of beta glucan, DL panthenol, grape seed extract, magnesium ascorbyl phosphate and superoxide dismutase.
[4] Blend C is a mixture of Blends A and B.
[5] This cell culture was exposed to UV light in the absence of added antioxidant materials.
[6] NSD is an abbreviation for Not Statistically Different.

As shown in Tables 1 and 2, Blends A and B provide statistically significant protection from the damaging effects of ultraviolet light in both the Percent Cellular Viability and PGE_2 production assays. As further shown in Tables 3 and 4, Blend C (which is composed of the ingredients in both Blends A and B) also showed statistically significant protection in these same tests when compared to cell cultures without the addition of the antioxidants.

Regarding the results obtained specifically from the Percent Cellular Viability assay method as shown in Table 5, Blend A was found to provide statistically better protection than Blend C. Blends A and B were not found to provide statistically different levels of protection by this method nor were Blends B and C found to provide statistically different levels of protection from the damaging effects of ultraviolet light. In the previous test procedure (see Table 1) the same relationship was found for Blends A and B.

The results obtained specifically from the PGE_2 Production assay method are shown in Table 6, which illustrates that Blend B was found to provide statistically better protection than Blend A. This is the same result found in the previous test (Table 2) where Blend B showed substantially greater reduction of PGE_2 production than Blend A. As shown in Tables 4 and 6, Blend C was found

to provide statistically better protection than Blend A. However, Blend B was also found to provide statistically better protection than Blend C by this assay for PGE_2 production.

TABLE 6

Statistical Comparison of PGE_2 Production Resulting from UV Light Exposure [1]

Antioxidant System	Blend B [3]	Blend C [4]	UV Irradiation Only [5]
Blend A [2]	95%	95%	95%
Blend B [3]	-	90%	95%
Blend C [4]	-	-	95%

[1] The values listed in this table are the statistical confidence level of difference based upon hypothesis testing using a Student t test.
[2] Blend A is composed of Vitamin A palmitate and Vitamin E acetate.
[3] Blend B is composed of beta glucan, DL panthenol, grape seed extract, magnesium ascorbyl phosphate and superoxide dismutase.
[4] Blend C is a mixture of Blends A and B.
[5] This cell culture was exposed to UV light in the absence of added antioxidant materials.

The fact that Blend A exhibits the best protection in the Percent Cellular Viability assay while Blend B exhibits the best protection in the PGE_2 Production assay may seem inconsistent. However, these two assays methods are different. The Reactive Oxygen Species (ROS) generated by ultraviolet light and that give rise to the damage detected by each assay method probably occurs from different biological pathways, thereby leading to different results. This explains why the water soluble antioxidants present in Blend B yield better protection in the PGE_2 production assay, whereas the oil soluble antioxidants present in Blend A yield better protection in the Percent Cellular Viability assay.

Blend A was also found to provide statistically better protection in the Percent Cellular Viability assay method as compared to Blend C, whereas Blend C was found to be statistically superior for the PGE_2 production assay. Similarly, although Blend B provides statistically better protection than Blend C in the PGE_2 Production assay, it is not statistically different from Blend C in the Percent Cellular Viability assay.

Although there are some statistical differences between the Blend C and blends of its oil or water soluble components, Blend C exhibits significant antioxidant activity in comparison to the individual ingredients tested previously.

Anyone skilled in the art of formulation will know how to readily incorporate these blends of antioxidant agents into suitable skin care and colored cosmetic products or into pharmaceutical products. Therefore, this information is intended to cover all possible combinations of these antioxidants in product formulations regardless of type or the market in which they are sold.

EXAMPLES 3 - 10

Protective Skin Compositions

These examples describe formulations to demonstrate the typical use of the protective skin composition of the present invention in skin care and over the counter (OTC) pharmaceutical products. These formulations are listed only as examples of the types of compositions that could be used, and are not all encompassing of the possible uses of the technology in skin care and OTC pharmaceutical products. One skilled in the art of formulation will readily envision other possible uses for this technology, and the invention is not restricted the use of the formulations listed below. All ingredients of the formulations listed below are shown in percentage by weight (% w/w).

EXAMPLE 3

Liquid Formulations

The following example is a general formula for liquid formulations of the composition.

Materials	General Use Range (Wt %)
Purified Water	19 - 98.7
Surfactants	0.5 - 5
Witch Hazel Distillate	0.01 -20
Humectant	0.5 - 5
Fragrance	0.001 - 1
Preservatives	0.2 - 3

Sequestering Agent	0.01 - 0.5
Menthol	0.005- 1
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.05 - 30
Magnesium Ascorbyl Phosphate	0.0001 - 3
Beta Glucan	0.005 - 5
Superoxide Dismutase	0.0001 - 1
Grape Seed Extract	0.00001- 1
Panthenol	0.005 - 5
Total	**100%**

EXAMPLE 4

Skin Toner

The following example is a formulation developed as a toner for the skin.

Materials	Specific Use Concentration (Wt %)
Purified Water	80
Surfactants	2
Witch Hazel Distillate	15
Humectant	1
Fragrance	0.035
Preservatives	1.9
Sequestering Agent	0.1
Menthol	0.01
Plant Extracts	0.07
Vitamin A Palmitate	0.005
Vitamin E Acetate	0.1
Magnesium Ascorbyl Phosphate	0.004
Beta Glucan	0.1
Superoxide Dismutase	0.004
Grape Seed Extract	0.0001
Panthenol	0.2
Total	**100%**

EXAMPLE 5

Oil-in-Water (O/W) Emulsion

The following example is a general formulation for an oil-in-water emulsion of a composition in accordance with the present invention.

Materials	General Use Range (Wt %)
Purified Water	0 - 98
O/W Emulsifiers	1 - 12
Humectants	0.5- 15
Fragrance	0.001 - 1
Preservatives	0.1 - 3
Sequestering Agent	0.01 - 0.5
Emollients	0.5 - 30
Thickeners	0.01 - 1
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.05- 30
Magnesium Ascorbyl Phosphate	0.0001-3
Beta Glucan	0.005- 5
Superoxide Dismutase	0.0001 - 1
Grape Seed Extract	0.00001- 1
Panthenol	0.005 - 5
Total	**100%**

EXAMPLE 6

Skin Moisturizing Lotion

The following example is an oil-in-water formulation developed as a moisturizing lotion for the skin.

Materials	Specific Use Concentration (Wt %)
Purified Water	80
O/W Emulsifiers	11
Humectants	5
Fragrance	0.05
Preservatives	2.7
Sequestering Agent	0.1
Emollients	12
Thickeners	0.3
Vitamin A Palmitate	0.05
Vitamin E Acetate	1
Magnesium Ascorbyl Phosphate	0.25
Beta Glucan	1
Superoxide Dismutase	0.04
Grape Seed Extract	0.005
Panthenol	2
Total	**100%**

EXAMPLE 7

Water-in-Oil (W/O) Emulsion

The following is a general formulation for a water-in-oil emulsion in accordance with some embodiments of the present invention.

Materials	General Use Range (Wt %)
Purified Water	0 - 98
W/O Emulsifiers	1- 10
Humectants	0 -10
Fragrance	0 - 0.5
Preservatives	0.1 - 7
Sequestering Agent	0.01 - 0.5
Emollients and Sunscreen Agents	10 - 60
Salt	0.01 - 1
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.05 - 30
Magnesium Ascorbyl Phosphate	0.0001 - 3
Beta Glucan	0.005 - 5
Superoxide Dismutase	0.0001 - 1
Grape Seed Extract	0.00001 - 1
Panthenol	0.005 – 5
Total	**100%**

EXAMPLE 8

Water-in-Oil Sunscreen Formulation

The following example is a formulation developed as a waterproof sunscreen product for the skin.

Materials	Specific Use Concentration (Wt %)
Purified Water	62
W/O Emulsifiers	6
Preservatives	3.65
Sequestering Agent	0.1
Emollients and Sunscreens Agents	27.75
Salt	0.3
Vitamin A Palmitate	0.005
Vitamin E Acetate	0.1
Magnesium Ascorbyl Phosphate	0.004
Beta Glucan	0.1

Superoxide Dismutase	0.004
Grape Seed Extract	0.0005
Panthenol	0.2
Total	**100%**

EXAMPLES 9 and 10

Synthetic (Moisturizing) Soap Bar

The following example is a general formulation for a moisturizing soap bar.

Materials	Example 9 General Use Range (Wt %)	Example 10 Specific
Purified Water	0 - 15	9.34
Detergents and Cleansing Agents	32 - 98	48.2
Buffering Agents	1 - 3	2.48
Humectants and Skin Conditioning Agents	0.5 - 5	13
Fragrance	0.001 - 1	0.24
Preservatives	0.01 - 2	0.09
Thickeners and Coloring Agents	0.01 - 30	25.67
Vitamin A Palmitate	0.0005 - 0.5	0.005
Vitamin E Acetate	0.05 - 30	0.5
Magnesium Ascorbyl Phosphate	0.0001 - 3	0.004
Beta Glucan	0.005 - 5	0.01
Superoxide Dismutase	0.0001 - 1	0.004
Grape Seed Extract	0.00001 - 1	0.195
Panthenol	0.005 - 5	0.195
Total	**100%**	**100%**

EXAMPLES 11 and 12

Waterproof SPF 20 Sunscreens

This example describes a waterproof SPF 20 formulation developed using a low level of sunscreens and the mixture of antioxidants in a water-in-oil emulsion. Example 11 provides examples of general ranges of ingredients, while Example 12 provides a specific formulation. In these Examples, Phases A and B represent an oil soluble phase, while Phase C is a water soluble phase.

	Example 11	Example 12
Phase A		
Abil WE-09 (Goldschmidt)	1 - 9%	5%
Ethylhexyl Methoxycinnamate	0.1 - 7.5%	3%
Oxybenzone	0.5 - 6%	2%
C12-15 alkyl benzoate	0.5 - 5%	2%
Octyl Palmitate	0.1 - 10%	4.5%
Octyl Stearate	0.1 - 8%	3%
Cetyl Dimethicone	0.01 - 5%	1%
Castorwax MP-80	0.01 - 4%	0.8%
Microcrystalline Wax	0.01 - 4%	1.2%
Phase B		
Vitamin E Acetate	0.0001 - 2%	0.1%
Vitamin A Palmitate	0.0001 - 2%	0.05%
Cyclomethicone 345	0.5 - 10%	5%
Phase C		
Water	to 100% - to 100%	to 100%
Magnesium Ascorbyl Phosphate	0.0001 - 2%	0.004%
Sodium Chloride	0.0001 - 2%	0.3%
Disodium EDTA	0.0001 - 1%	0.1%
Beta Glucan	0.0001 - 1%	0.1%
Grape Seed Extract	0.0001 - 1%	0.5%
Superoxide Dismutase	0.0001 - 1%	0.004%
Fragrance and Preservatives	q.s.[1] q.s.	q.s.
Total	**100% 100%**	**100%**

[1] q.s. is an abbreviation for quantity sufficient

Mixing Procedure: The ingredients of Phase A were mixed in a container, and heated with mixing to 80 to 85°C until all the waxes melted. Then heating was discontinued, and the mixture cooled to 50 to 55°C. The ingredients of Phase B were also mixed in a container at room temperature until uniform, while trying to avoid entrapment of air by mixing slowly without creating a vortex. The mixture of Phase B was added to the mixture of Phase A and mixed thoroughly, again while avoiding entrapment of air.

The ingredients of Phase C were mixed in an appropriate container, and heated with mixing to 45 to 50°C until all solid materials were completely dissolved. With slow but thorough mixing, Phase AB was added at 55 to 60°C to

Phase C at 45 to 50°C. After completion of the addition, the batch was homogenized while maintaining a temperature of 45 to 50°C. After homogenization, the mixing was continued while beginning cooling to 30°C. Once at room temperature, the batch was packaged in appropriate containers.

The formulation exhibited a waterproof SPF of greater than 17.9 on five subjects. The formulation without the sunscreen agents, but with antioxidants, exhibited a waterproof SPF of only 2.8 on the same 5 subjects. The expected SPF for this combination of sunscreen agents alone would be less than 8, although the exact value was not determined. If the expected SPF of the sunscreen agents alone is added to the SPF resulting from the antioxidants, the total SPF (~ 10.8) is only 60% of that found for the resulting product.

EXAMPLE 13

Waterproof SPF 30 sunscreen

This example describes a waterproof SPF 30 formulation developed using a low level of sunscreens and the mixture of antioxidants in a water-in-oil emulsion. All percentages are by weight. Phases A and B are oil soluble and Phase C is water soluble.

Phase A	
Abil WE-09 (Goldschmidt)	8%
Ethylhexyl Methoxycinnamate	7%
Ethylhexyl Salicylate	3%
Oxybenzone	2%
C12-15 alkyl benzoate	6%
Octyl Palmitate	5%
Cetyl Dimethicone	1%
Castorwax MP-80	0.8%
Microcrystalline Wax	1.2%
Phase B	
Vitamin E Acetate	0.1%
Vitamin A Palmitate	0.05%
Cyclomethicone 345	1%
Phase C	
Water	to 100%
Magnesium Ascorbyl Phosphate	0.004%
Sodium Chloride	0.3%
Disodium EDTA	0.1%

Beta Glucan (Camamino)	0.1%
Grape Seed Extract	0.5%
Superoxide Dismutase	0.004%
Fragrance and Preservatives	q.s.
Total	**100%**

The composition was mixed in the same manner as described in Examples 11 and 12.

The formulation of Example 13 exhibited a waterproof SPF of greater than 32.1 on five subjects. The same formulation without the antioxidants (Vitamins A, C and E, Beta Glucan, Grape Seed Extract and Superoxide Dismutase) exhibited a waterproof SPF of 19.6 on the same 5 subjects. The formulation without the sunscreen agents but with antioxidants exhibited a waterproof SPF of 2.8. The sum of the SPF values of the individual components of this product (22.4) is only about 70% of the SPF value found for the complete product tested separately. This measured SPF is also 40% greater than the expected 22.4 SPF (32.1 – 22.4 = 9.7, which is 43% of the expected 22.4 SPF).

The present invention takes advantage of the surprising superiority found when combining two skin agents that protect the skin from ultraviolet radiation, one agent from a class of protectants that increases cellular viability, and the other from a class that decreases the production of PGE_2 in the skin, as measured by the assays of Example 1. In addition, the present invention also takes advantage of the result that a mixture of antioxidants and sunscreen agents synergistically combine in a water-in-oil emulsion to provide unexpectedly superior protection to the skin against the harmful effects of ultraviolet radiation. The compositions of the invention can be applied to skin both before or after exposure to ultraviolet radiation, to provide the protective effect, however application before exposure to the sun is preferred. Daily applications of the skin protectant may be used, even if exposure to the sun is not anticipated, to diminish the aging effects of ROS in the skin. The invention explicitly includes the mixture of antioxidants, either with or without the water-in-oil emulsion.

As used in this specification, reducing damage caused by exposure to ultraviolet radiation means reducing damage as measured by the assays of

Example 1 (increased epidermal cellular viability) or Example 2 (reduced PGE_2 production by epidermal cells). Ultraviolet radiation refers to electromagnetic radiation having a wavelength shorter than the wavelengths of visible light and longer than those of x-rays. Skin injury refers to cellular damage as measured by decreased cellular viability or increased PGE_2 production, or both. An antioxidant is a substance that opposes the effects of ROS, either by scavenging or reducing ROS, or interfering with the production of ROS.

Possible surfactants include polyoxyethylene sorbitan esters of fatty organic acids (such as laureate, palmitate, stearate, oleate and myristate) containing various molar concentrations of ethylene oxide (commonly listed as polysorbate 20, 21, 40, 60, 61, 65, 80, 81 and 85) as well as combinations of these ingredients.

Possible humectants include sugars (such as sorbitol, glucose, etc.), glycerin (and its polymers), glycols (such as propylene glycol, butylene glycol, and polyethylene glycols of various molecular weights), hyaluronic acid (and its salts), pyrrolidone carboxylic acid (and its salts) as well as combinations of these ingredients.

Possible preservatives include the parabens (such as the methyl, ethyl, propyl, isopropyl, butyl and isobutyl esters), imidazolidinyl urea, diazolidinyl urea, quaternium-15, phenylethyl alcohol, benzyl alcohol, phenoxyethanol, chlorphenesin, chlorhexidine digluconate as well as combinations of these ingredients.

Possible sequestering agents include the various salts of ethylenediamine tetraacetic acid (sodium, potassium, amine and amino acid salts).

Magnesium ascorbyl phosphate is a stabilized form of Vitamin C.

Stabilized forms of Vitamin A can be used in the preferred embodiment of the invention, such as the alcohol retinol or any of its esters. Other forms (such as Retin A) could also be used, but are less stable. Vitamin E is preferably used in its alcohol form (tocopherol), or any of its esters, or other stabilized forms.

Possible O/W surfactants include the salts of fatty acids (such as sodium, potassium, amine or amino acid salts of stearic, myristic, oleic, lauric or palmitic

acid), non-ionic surfactants such as the polysorbates listed above, sorbitan esters of fatty acids (such as stearates, myristates, oleates, laureates, and palmitates), glyceryl esters of fatty acids (stearate, myristate, oleate, laureate and palmitate), polyoxyethylene esters of lanolin acids, alcohols and other wool wax components, polyoxyethylene ethers of fatty alcohols (such as lauryl, cetyl, oleyl and stearyl), polyethylene glycol esters of fatty acids (such as laureate, stearate, myristate, oleate, and palmitate), homo- and mixed block polymers of polyoxyethylene and polyoxypropylene, polyoxypropylene esters of fatty acids, polyoxypropylene ethers of fatty alcohols, sugar esters of fatty acids (such as the fatty acid esters of glucose and sucrose) and quaternary amine salts of fatty acids as well as combinations of these ingredients chosen to yield an oil-in-water emulsion.

Possible emollients include esters of fatty acids and fatty alcohols (such as octyl palmitate, octyl stearate, cetearyl stearate, etc.), silicone compounds (such as dimethicone, cyclomethicone, phenyltrimethicone, etc.), esters of organic acids and organic alcohols (C12-15 alkyl benzoate, octyl dodecanol, cetyl lactate, tridecyl trimellitate, octyldodecyl neopentanoate, etc.), fatty alcohols (cetyl alcohol, stearyl alcohol, etc.), castor oils, fractions of castor oils and their hydrogenated derivatives as well as combinations of these types of ingredients.

Possible thickeners include acrylic acid polymers and their cross polymer derivatives, polyvinylpyrrolidone polymers, natural polymers (such as locus bean gum, xanthan gum, alginic acid and its salts, dextran, etc.), clays (hectorite, montmorillonite, etc.) as well as combinations of these ingredients.

Possible water-in-oil (W/O) emulsifiers include the appropriate combinations of the oil-in-water emulsifiers listed above as well as cetyl dimethicone copolyols and other various other dimethicone copolyols in addition to combinations of these ingredients.

Possible emollients and sunscreens include the emollients listed above, as well as any approved sunscreen agents such as dioxybenzone, homomenthyl salicylate, menthyl anthranilate, octocrylene, octyl methoxycinnamate, octyl paraaminobenzoate, octyl salicylate, oxybenzone, and trolamine salicylate, as well as combinations of these ingredients.

Possible salts include sodium chloride, potassium chloride, lithium chloride and magnesium chloride or combinations of these ingredients.

Possible detergents and cleansing agents include the salts of cocyl isethionate, isostearoyl lactylate salts (such as the sodium and potassium salts), tallow and tallow salts (such as sodium, potassium and ammonium salts), salts of lauryl and laureth sulfates (such as sodium, potassium and ammonium salts), betaines and sultaines (such as cocamidopropyl betaine or sultaine) and salts of fatty acids (such as sodium or potassium laureate, myristate, palmitate, stearate, oleate, behenate, linoleate and ricinoleate) as well as combinations of these ingredients.

Possible buffering agents include all conventional buffering systems use in chemistry but especially lactic acid combined with a salt of lactic acid (such as sodium lactate) in appropriate ratios to maintain a given pH value.

Possible humectants and skin conditioning agents include the humectants listed above, salts of isostearoyl lactylate (such as sodium or potassium), quaternium compounds (such as stearamidopropyl dimethylamine) and oat by-products (such as oat flour) as well as combinations of these ingredients.

Possible thickeners and colorants include those thickeners listed above (see footnote 8) and colorants such as titanium dioxide, iron oxides, FD&C and D&C colorants, ultramarine blue, carmine, annatto, chlorophyll and other natural or artificial colorants as well as combinations of these ingredients.

In view of the many possible embodiments to which the principles of our invention may be applied, it should be recognized that the illustrated embodiments are only specific examples of the invention and should not be taken as a limitation on the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within the scope and spirit of these claims.

We claim:

1. A method of inhibiting skin damage induced by ultraviolet radiation, the method comprising:

applying topically to the skin a composition comprising beta glucan in a sufficient amount to reduce skin damage caused by exposure to ultraviolet radiation.

2. The method of claim 1, wherein the composition further comprises panthenol, grape seed extract, Vitamin C, and superoxide dismutase.

3. The method of claim 1, wherein the composition further comprises Vitamin A and Vitamin E.

4. The method of claim 1, wherein the composition comprises at least about 0.005% beta glucan.

5. The method of claim 4, wherein the composition comprises about 0.005-5% beta glucan.

6. The method of claim 2, wherein the composition comprises at least about 0.005% panthenol, 0.00001% grape seed extract, 0.0001% Vitamin C, and 0.0001% superoxide dismutase.

7. The method of claim 6, wherein the composition comprises about 0.005-5% panthenol, 0.00001-1% grape seed extract, 0.0001-3% Vitamin C, and 0.0001-1% superoxide dismutase.

8. The method of claim 7, wherein the composition further comprises at least about 0.0005% Vitamin A, and at least 0.05% Vitamin E.

9. The method of claim 8, wherein the composition comprises about 0.0005-0.5000% Vitamin A and 0.0500-30% Vitamin E.

10. The method of claim 1, further comprising applying a mixture of one or more sunscreen agents and one or more antioxidants to the skin prior to exposure to ultraviolet radiation, wherein the mixture also contains a polyorganosiloxane emulsifier that enhances an SPF of the mixture.

11. The method of claim 1, wherein the composition is provided in an emulsion that enhances an SPF of the composition.

12. The method of claim 2, wherein the composition is provided in an emulsion that enhances an SPF of the composition.

13. The method of claim 3, wherein the composition is provided in an emulsion that enhances an SPF of the composition.

14. The method of claim 1, wherein the composition is provided in an emulsion that enhances an SPF of the composition.

15. The method of claim 1, wherein the emulsion is a polyorganosiloxane emulsion.

16. A topical composition for reducing skin damage induced by ultraviolet radiation, the composition comprising:

beta glucan in a sufficient amount to reduce the skin damage when applied topically; and

at least one other skin protectant that reduces the skin damage caused by ultraviolet light.

17. The topical composition of claim 16, wherein the other skin protectant is selected from the group consisting of one or more of panthenol, grape seed extract, Vitamin C and superoxide dismutase in a sufficient amount to reduce production of PGE_2, or increase cellular viability, in the skin when applied topically.

18. The composition of claim 16, wherein the composition further comprises an antioxidant selected from the group consisting of one or both of Vitamin A and Vitamin E in a sufficient amount to reduce reactive oxygen species in the skin when applied topically.

19. The topical composition of claim 17, wherein the composition comprises about 0.005-5% beta glucan, 0.005-5% panthenol, 0.00001-1% grape seed extract, 0.0001-3% Vitamin C, and 0.0001-1% superoxide dismutase.

20. The topical composition of claim 17, wherein the composition comprises about 0.0005-0.5000% Vitamin A and 0.0500-30% Vitamin E.

21. The topical composition of claim 17, wherein the composition further comprises at least about 0.0005% Vitamin A, and at least 0.01% Vitamin E.

22. The topical composition of claim 19, wherein the Vitamin C is in the form of magnesium ascorbyl phosphate.

23. The topical composition of claim 20, wherein the Vitamin A is in the form of Vitamin A palmitate and the Vitamin E is in the form of Vitamin E acetate.

24. The topical composition of claim 17, wherein the other skin protectant is a protectant that improves cellular viability following exposure to ultraviolet radiation.

25. The topical composition of claim 18, further comprising a sunscreen, and an emulsifier in a sufficient amount to enhance an SPF of the composition.

26. The topical composition of claim 23, wherein the emulsifier is a water-in-oil polyorangosiloxane emulsifier.

27. The topical composition of claim 16, wherein the composition further comprises an antioxidant that includes lipid soluble and water soluble components; a sunscreen; and an emulsifier to emulsify a sufficient amount of the antioxidant and the sunscreen to provide a sun-protective composition.

28. A topical composition for protecting skin against damage from ultraviolet radiation, comprising:

beta glucan, panthenol, grape seed extract, Vitamin C and superoxide dismutase in a sufficient amount to increase cellular viability and reduce the production of PGE_2 in the skin to which the composition is applied, that is exposed to ultraviolet radiation.

29. The topical composition of claim 28, further comprising Vitamin A and Vitamin E in sufficient amounts to have an antioxidant effect on the skin when topically applied.

30. The composition of claim 28, wherein the composition comprises by weight about:

0.005-5% beta glucan;

0.005-5% panthenol;

0.00001-1% grape seed extract;

0.0001-3% Vitamin C; and

0.0001-1% superoxide dismutase.

31. The composition of claim 28, comprising by weight at least about:

0.005% beta glucan;

0.005% panthenol;

0.00001% grape seed extract;

0.0001% Vitamin C; and

0.0001% superoxide dismutase.

32. The composition of claim 31, further comprising by weight at least about 0.0005% Vitamin A, and at least 0.05% Vitamin E.

33. The composition of claim 32, further comprising by weight about:

0.0005-0.5000% Vitamin A; and

0.0100-30% Vitamin E.

34. The composition of claim 16, in an aqueous or non-aqueous solution, suspension, a water-in-oil or oil-in-water emulsion.

35. The composition of claim 16 in a skin toner composition, a moisturizing lotion, a sunscreen composition, a skin cleanser or other skin treatment composition.

36. A topical antioxidant composition comprising a first component that increases cellular viability of epidermal cells, and a second component that decreases the production of PGE_2.

37. A composition comprising:

an antioxidant that includes lipid soluble and water soluble components;

a sunscreen; and

an emulsifier to emulsify a sufficient amount of the antioxidant and the sunscreen to provide a sun-protective composition.

38. The composition of claim 37, wherein the emulsifier is a polyorganosiloxane emulsifier that enhances a sun protection factor (SPF) of the composition.

39. The composition of claim 37, wherein the composition comprises a low level of sunscreen agent in the sunscreen, and the antioxidant comprises a mixture of antioxidants in a water-in-oil polyorganosiloxane emulsion.

40. A composition of claim 37 in which the sunscreen comprises one or more agents selected from the group of: ethylhexyl methoxycinnamate, DEA methoxycinnamate, Padimate O, ethylhexyl salicylate, homosalate, TEA salicylate, oxybenzone, dioxybenzone, sulisobenzone, avobenzone, octocrylene, titanium dioxide, zinc oxide or menthyl anthranilate.

41. The composition of claim 37, wherein the sunscreen comprises at least one UVA sunscreen agent selected from the group of oxybenzone, dioxybenzone, sulisobenzone, avobenzone or zinc oxide, and at least one UVB sunscreen agent, selected from the group of ethylhexyl methoxycinnamate, DEA methoxycinnamate, Padimate O, ethylhexyl salicylate, homosalate, TEA salicylate, octocrylene or titanium dioxide.

42. The composition of claim 37, wherein the sunscreen comprises at least oxybenzone and at least one of ethylhexyl methoxycinnamate and octyl salicylate.

43. The composition of claim 37 in which the lipid soluble component of the antioxidant comprises one or both of Vitamins and A and E.

44. The composition of claim 37 in which the water soluble component of the antioxidant comprises one or more antioxidants selected from the group of magnesium ascorbyl phosphate, DL panthenol, beta glucan, grape seed extract and superoxide dismutase.

45. The composition of claim 37 in which the antioxidant comprises a mixture of antioxidants comprising Vitamins A and E or their esters, magnesium ascorbyl phosphate, DL panthenol, beta glucan, grape seed extract and superoxide dismutase.

46. The composition of claim 37, wherein the composition is at least 50% water, and the emulsifier includes 1-12% of an emulsification system that includes cetyl dimethicone copolyol, and the sunscreen agent and antioxidant are present in an amount sufficient to maintain the SPF of the composition at a value greater than about 15.

47. The composition of claim 37, wherein the sum of the SPF values of the antioxidant and sunscreen components tested separately is no more than about 70% of the SPF value of the sunscreen components tested together.

48. A method of improving an SPF value of a formulation for protecting skin from harmful effects of ultraviolet radiation, comprising combining one or more lipid soluble antioxidants with one or more water soluble antioxidants and one or more sunscreen agents, in the presence of an organopolysiloxane emulsifier, the formulation having the antioxidants, sunscreen agents and emulsifier present in an amount sufficient to enhance the SPF value of the formulation to greater than the sum of the SPF value of the antioxidants and sunscreen agents apart.

49. An ultraviolet radiation protective composition, comprising about 0.0002-4% of a lipid soluble sunscreen component that includes Vitamin A and Vitamin C; about 0.004-5% of a water soluble sunscreen component that includes Vitamin C, beta glucan, grape seed extract, and superoxide dismutase; an emulsifier; and a sunscreen component that contains less than about 12% of an non-particulate sunscreen agent that is substantially free of metal oxides.

50. The composition of claim 49, wherein the emulsifier comprises a polyalkylsiloxane.

51. The composition of claim 49, wherein the emulsifier further comprises a fatty alcohol.

52. The composition of claim 49, wherein the emulsifier comprises polyglyceryl-4-isostearate, cetyl dimethicone copolyol, and hexyl laurate.

53. A composition comprising about:

Primary emulsifier	1 - 9%
Ethylhexyl Methoxycinnamate	0.1 - 7.5%

Oxybenzone	0.5 - 6%
C12-15 alkyl benzoate	0.5 - 5%
Octyl Palmitate	0.1 - 10%
Octyl Stearate	0.1 - 8%
Cetyl Dimethicone	0.01 - 5%
Castorwax MP-80	0.01 - 4%
Microcrystalline Wax	0.01 - 4%
Vitamin E Acetate	0.0001 - 2%
Vitamin A Palmitate	0.0001 - 2%
Cyclomethicone	0.5 - 10%
Water	to 100% to 100%
Magnesium Ascorbyl Phosphate	0.0001 - 2%
Sodium Chloride	0.0001 - 2%
Disodium EDTA	0.0001 - 1%
Beta Glucan	0.0001 - 1%
Grape Seed Extract	0.0001 - 1%
Superoxide Dismutase	0.0001 - 1%
Fragrance and Preservatives	q.s.[1] q.s.
Total	**100% 100%**

wherein the primary emulsifier comprises cetyl dimethicone colpolyol.

54. The composition of claim 53, comprising about:

Primary emulsifier	5%
Ethylhexyl Methoxycinnamate	3%
Oxybenzone	2%
C12-15 alkyl benzoate	2%
Octyl Palmitate	4.5%
Octyl Stearate	3%
Cetyl Dimethicone	1%
Castorwax MP-80	0.8%
Microcrystalline Wax	1.2%
Vitamin E Acetate	0.1%
Vitamin A Palmitate	0.05%
Cyclomethicone	5%
Water	to 100%
Magnesium Ascorbyl Phosphate	0.004%
Sodium Chloride	0.3%
Disodium EDTA	0.1%
Beta Glucan	0.1%
Grape Seed Extract	0.5%
Superoxide Dismutase	0.004%
Fragrance and Preservatives	q.s.
Total	**100%**

or

Primary emulsifier	8%

Ethylhexyl Methoxycinnamate	7%
Ethylhexyl Salicylate	3%
Oxybenzone	2%
C12-15 alkyl benzoate	6%
Octyl Palmitate	5%
Cetyl Dimethicone	1%
Castorwax MP-80	0.8%
Microcrystalline Wax	1.2%
Vitamin E Acetate	0.1%
Vitamin A Palmitate	0.05%
Cyclomethicone	1%
Water	to 100%
Magnesium Ascorbyl Phosphate	0.004%
Sodium Chloride	0.3%
Disodium EDTA	0.1%
Beta Glucan (Camamino)	0.1%
Grape Seed Extract	0.5%
Superoxide Dismutase	0.004%
Fragrance and Preservatives	q.s.
Total	**100%**

wherein the primary emulsifier further comprises polyglyceryl-4-isostearate and hexyl laurate.

55. The composition of claim 53 wherein the primary emulsifier comprises polyglyceryl-4- isostearate, cetyl dimethicone copolyol and hexyl laurate.

56. A composition comprising about:

(a)

	Percent by weight
Purified Water	19 - 98.7
Surfactants	0.5 - 5
Witch Hazel Distillate	0.01 - 20
Humectant	0.5 - 5
Fragrance	0.001 - 1
Preservatives	0.2 - 3
Sequestering Agent	0.01 - 0.5
Menthol	0.005- 1
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.05 - 30
Magnesium Ascorbyl Phosphate	0.0001 - 3
Beta Glucan	0.005 - 5
Superoxide Dismutase	0.0001 - 1

Grape Seed Extract	0.00001- 1
Panthenol	0.005 - 5
Total	**100%**

or (b)

	Percent by weight
Purified Water	0 - 98
O/W Emulsifiers	1 - 12
Humectants	0.5 - 15
Fragrance	0.001 - 1
Preservatives	0.1 - 3
Sequestering Agent	0.01 - 0.5
Emollients	0.5 - 30
Thickeners	0.01 - 1
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.05 - 30
Magnesium Ascorbyl Phosphate	0.0001 - 3
Beta Glucan	0.005 - 5
Superoxide Dismutase	0.0001 - 1
Grape Seed Extract	0.001 - 1
Panthenol	0.005 - 5
Total	**100%**

or (c)

	Percent by weight
Purified Water	0 - 98
W/O Emulsifiers	1- 10
Humectants	0 - 10
Fragrance	0 - 0.5
Preservatives	0.1 - 7
Sequestering Agent	0.01 - 0.5
Emollients and Sunscreen Agents	10 - 60
Salt	0.01 - 1
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.01 - 30
Magnesium Ascorbyl Phosphate	0.0001 - 3
Beta Glucan	0.005 - 5
Superoxide Dismutase	0.0001 - 1
Grape Seed Extract	0.001 - 1
Panthenol	0.005 - 5
Total	**100%**

or (d)

	Percent by weight
Purified Water	0 - 15
Detergents and Cleansing Agents	32 - 98
Buffering Agents	1 - 3
Humectants and Skin Conditioning Agents	0.5 - 5
Fragrance	0.001 - 1
Preservatives	0.01 - 2
Thickeners and Coloring Agents	0.01 - 30
Vitamin A Palmitate	0.0005 - 0.5
Vitamin E Acetate	0.01 - 30
Magnesium Ascorbyl Phosphate	0.0001 - 3
Beta Glucan	0.005 - 5
Superoxide Dismutase	0.0001 - 1
Grape Seed Extract	0.001 - 1
Panthenol	0.005 - 5
Total	**100%**

or (e)

	Percent by Weight
Purified Water	9.34
Detergents and Cleansing Agents	48.2
Buffering Agents	2.48
Humectants and Skin Conditioning Agents	13
Fragrance	0.24
Preservatives	0.09
Thickeners and Colorants	25.66
Vitamin A Palmitate	0.005
Vitamin E Acetate	0.49
Magnesium Ascorbyl Phosphate	0.004
Beta Glucan	0.01
Superoxide Dismutase	0.004
Grape Seed Extract	0.195
Panthenol	0.195
Total	**100%**

or (f)

	Percent by weight
Purified Water	80
O/W Emulsifiers	11
Humectants	5
Fragrance	0.05
Preservatives	2.7
Sequestering Agent	0.1
Emollients	12

Thickeners	0.3
Vitamin A Palmitate	0.05
Vitamin E Acetate	1
Magnesium Ascorbyl Phosphate	0.25
Beta Glucan	1
Superoxide Dismutase	0.04
Grape Seed Extract	0.005
Panthenol	2
Total	**100%**

or (g)

	Percent by weight
Purified Water	80
Surfactants	2
Witch Hazel Distillate	15
Humectant	1
Fragrance	0.035
Preservatives	1.9
Sequestering Agent	0.1
Menthol	0.01
Plant Extracts	0.07
Vitamin A Palmitate	0.005
Vitamin E Acetate	0.1
Magnesium Ascorbyl Phosphate	0.004
Beta Glucan	0.1
Superoxide Dismutase	0.004
Grape Seed Extract	0.0001
Panthenol	0.2
Total	**100%**

57. A sunscreen product for the skin, comprising about:

	Percent by weight
Purified Water	62
W/O Emulsifiers	6
Preservatives	3.65
Sequestering Agent	0.1
Emollients and Sunscreens Agents	27.75
Salt	0.3
Vitamin A Palmitate	0.005
Vitamin E Acetate	0.1
Magnesium Ascorbyl Phosphate	0.004
Beta Glucan	0.1
Superoxide Dismutase	0.004
Grape Seed Extract	0.0005

Panthenol	0.2
Total	**100%**

58. Any of the compositions of claim 56, further comprising a suncreen agent, and apolyorganosiloxane water-in-oil emulsion that increases an SPF of the composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/27433

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61K 7/42, 7/44
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPATFULL online
CAS online

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,505,935 A (GUERRERO et al) 09 April 1996, columns 5 and 6 inclusive.	1-58

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
01 MARCH 1999	16 MAR 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JAMES O. WILSON Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet)(July 1992)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/27433

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

424/59, 60
514/ 772, 772.3, 772.4, 844, 847, 937, 938

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

424/59, 60
514/ 772, 772.3, 772.4, 844, 847, 937, 938